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著者	OBINATA Ichiji, KOMATSU Noboru
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Method of Refining Silicon by Alloying*

Ichiji OBINATA and Noboru KOMATSU

The Research Institute for Iron, Steel and Other Metals

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Synopsis

For refining crude silicon, a new method consisting essentially of electrolysis of Al-Si anode obtained by alloying crude silicon into molten aluminium was proposed. The principles of the method as well as the results of observations on the behavior of the impurities contained in the crude silicon during the process are described. As a plan for carrying out the present refining method in practice, the flow-sheet is shown in Fig. 8, with the aim of estimating the quantity and the cost of the materials required in practical application of this purifying method.

The impurities contained in the purified silicon were found to be as follows: Al: 0.18, Fe: 0.003, Ca: trace, C: 0.022, Ti: 0.001, and P: 0.003 in per cent. The quantity of several materials, chemicals and the electric power as well as their cost were estimated in order to produce 1 kg of purified silicon.

I. Introduction

The usual method of fabricating metallic silicon is to reduce silica by solid carbon at high temperature. The purity of metallic silicon thus obtained is usually between 96 and 98 weight per cent. Some other method should, therefore, be required in order to obtain silicon of high purity.

There is a method called Tucker's[(1)] of treating pulverized silicon with HCl, HNO_3 and HF for eliminating the impurities. The silicon up to the purity of 99.7~99.9 per cent may be obtained by this method. The other methods proposed are of the chloride process resembling to the Kroll's process for refining titanium. In these methods, crude silicon is chlorinated into silicon tetrachloride, purified and then reduced with zinc and magnesium. Although silicon of the highest purity may be obtained by such a method, there are many difficulties in carrying out the process, resulting in an inconveniently high cost[(2)]. The present authors have derived a simple purifying method of silicon starting from an idea utterly different from the above. The fundamental studies and semi-industrial tests of this method have been carried out.

II. Fundamental research

1. Fundamental principles of new method

During the metallographic researches on Al-alloys, the present authors came upon the observation that the silicon crystallized primarily in Al-Si alloys was of

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* The 871st report of the Research Institute for Iron, Steel and Other Metals.

(1) N. P. Tucker, J. Iron and Steel Institute, **115** (1927), 412.

(2) K. Ono and T. Matsushima, The Bulletin of the Research Institute of Mineral Dressing and Metallurgy, **8** (1952), 89.

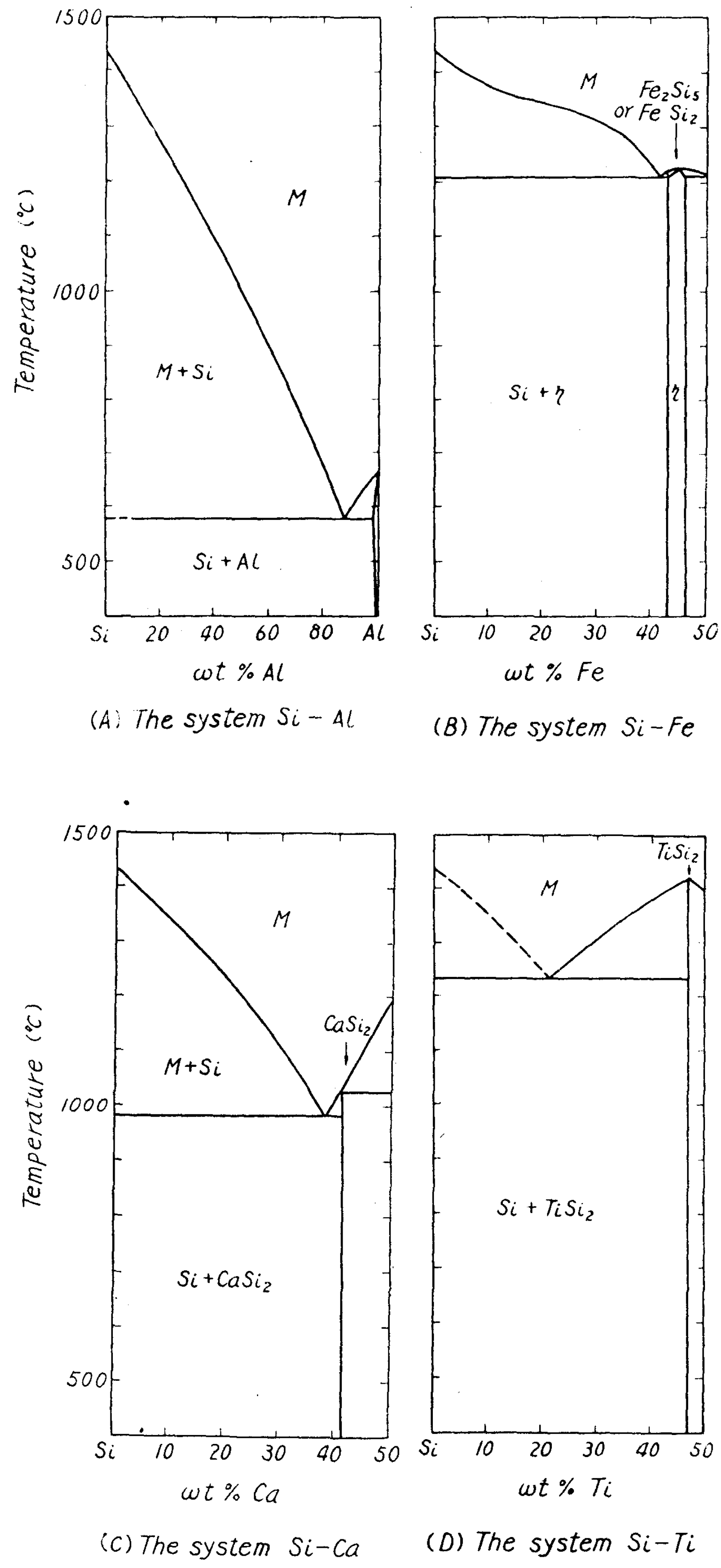

Fig. 1. Equilibrium diagrams of the binary alloys of silicon.

rather high purity, and were led to consider the possibility of obtaining such high purity silicon from Al-Si alloys.

In equilibrium diagram of Al-Si binary system shown in Fig. 1(A)(3), the solubility of aluminium in solid silicon is not yet comfirmed exactly. According to W. Broniewski and M. Smialowski, it is about 4 per cent at the eutectic temperature. Later on, however, W. L. Fink and K. R. van Horn pointed out that this value was too high(3). According to the present experiments it was about 0.2 per cent. (Table 5)

The chief impurities contained in crude silicon are iron, aluminium, calcium, carbon, titanium and phosphorus as shown in Table 1. When crude silicon of such purity is alloyed in aluminium, the above-mentioned impurities will either melt into aluminium or separate out unalloyed.

Table 1. Composition limits of crude silicon (Metals Handbook).

Al	Fe	Ca	C	Ti	P	Si
0.1~0.3	bal.	0.2~0.5	0.03~0.3	0.1~0.2	0.01~0.05	96~98

Iron: In silicon, iron takes the form of $FeSi_2$ or Fe_2Si_5, as shown in Fig. 1 (B)(4). When crude silicon containing iron is alloyed with aluminium, the ternary compound Al_4FeSi may be formed as shown in Fig. 2(5).

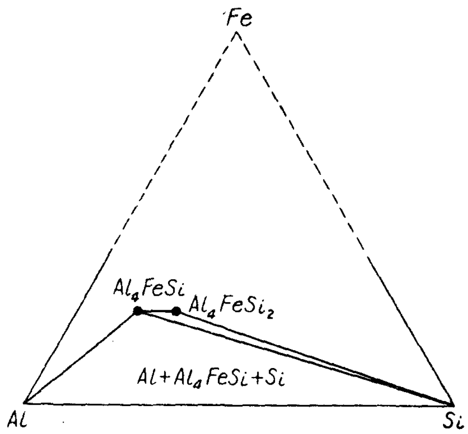

Fig. 2. The system Al-Fe-Si(5).

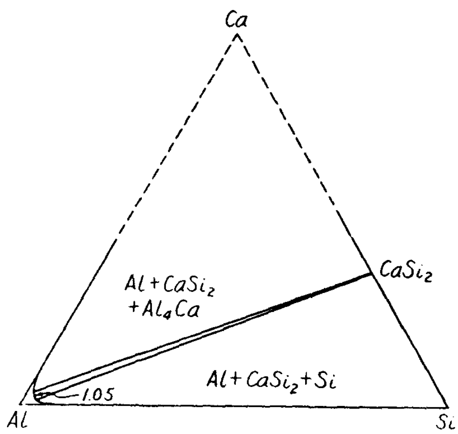

Fig. 3. The system Al-Ca-Si(7).

Calcium: The equilibrium diagram of the system Ca-Si is shown in Fig. 1 (C)(6), calcium being mechanically mixed with silicon as $CaSi_2$. When alloyed with aluminium, a part of $CaSi_2$ may be dissociated and it will dissolve in aluminium as a solid solution up to 1.5 per cent Ca, as shown in Fig. 3(7).

(3) W. L. Fink & L. A. Willey, Metals Handbook (1948), A. S. M.
(4) R. L. Rickett, Metals Handbook (1948), A. S. M.
(5) I. Obinata & N. Komatsu, Nippon Kinzoku Gakkai-Shi, **17** (1953), A-12.
(6) M. Hansen, Aufbau der Zweistofflegierungen, Berlin, Springer (1936).
(7) M. Hanemann u. A. Schrader, Ternäre Legierungen der Aluminiums. (1952). Atlas Metallographicus III, 2.

Carbon: The equilibrium relation between silicon and carbon is unknown, but it may be presumed that it is a mechanical mixture of the form of SiC. It is also unknown how this SiC will behave when alloyed with aluminium, but as the temperature of the aluminium melt is not high, a part of it presumably will come out as slag, without being alloyed.

Titanium: Titanium in silicon mechanically mixes with silicon in the form of $TiSi_2$, as shown in Fig. 1(D)[8]. When alloyed with aluminium, titanium will probably dissolve in solid solution of aluminium.

Phosphorus: The equilibrium relations of phosphorus to aluminium and silicon are yet known, but it has been pointed out, according to the recent researches on silumin by Gürtler et al.,[10][11] that in hypereutectic Al-Si alloys, particles of Al_3P act as nuclei for primary silicon crystals to grow on. Consequently, a part of phosphorus in silicon may dissolve in molten aluminium.

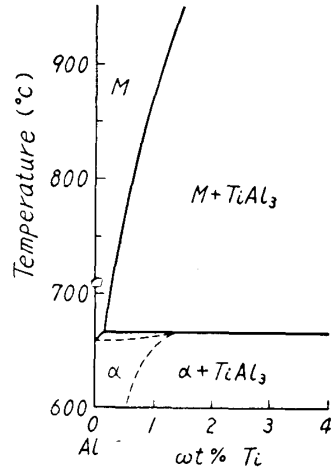

Fig. 4. The system Al-Ti[9].

If the above inferences are right, by alloying crude silicon with aluminium, a part of its impurities, e. g., carbon will be eliminated without being alloyed, and another part, including calcium, titanium etc. can be collected as solid solutions of aluminium, while iron will form a separate phase of Al-Fe-Si ternary compounds mixed mechanically with aluminium and silicon.

As aluminium is a chemically active element, if hypereutectic Al-Si alloy is treated with strong acid such as hydrochloric acid, the solid solutions of aluminium will be easily dissolved out. On the other hand, as silicon is inactive against strong acid, the crystals of silicon in the alloy can, then, be collected as slime. Here, iron alone may possibly be found remaining in the slime in the form of Al-Fe-Si compounds, but the following experiments revealed the easiness of separating such compounds.

2. Experimental method and results

(i) Alloying crude silicon with aluminium

Aluminium, 99.5 per cent purity, was melted in an alumina-lined graphite crucible. Crude silicon of the composition shown in Table 2 was added to it bit by bit, and while raising the temperature of the melt, the prescribed quantity of silicon was alloyed in it. The quantity of silicon added is shown in Table 3, the total quantity of the alloys melted being 400 g in every case. The specimens were cast in dry sand molds preheated at 100°C, and two cylindrical rods, 20 mm in diameter and 20 cm in length, were prepared.

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(8) M. Hansen, H. D. Kessler & D. J. McPherson, Trans. A. S. M., **44** (1952), 518.

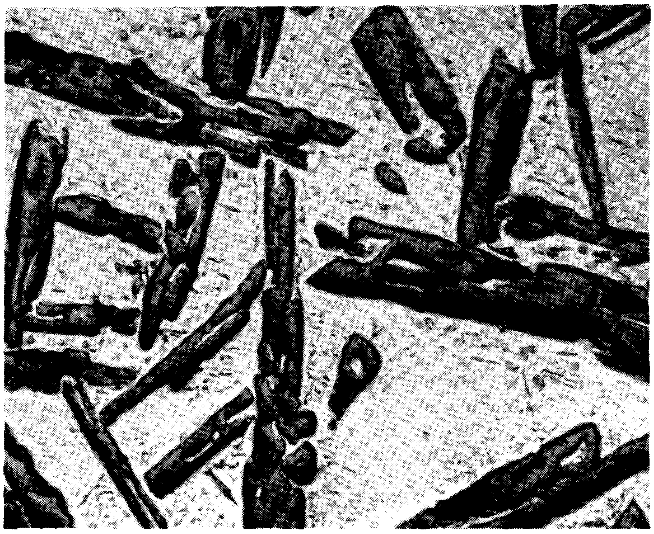
Table 2. Compositions of crude Si, Al-Si alloys prepared, extracted silicon and purified silicon.

Materials	Al	Fe	Ca	C	Ti	P	Si
Crude Si	0.29	0.31	0.29	0.093	0.026	0.012	bal.
Sp. No. 1	bal.	0.26	0.000	0.005	0.006	0.002	30.30
Sp. No. 2	bal.	0.24	0.005	0.000	0.015	0.009	40.39
Sp. No. 5	bal.	0.49	0.14	0.012	0.016	0.030	70.16
Sp. No. 6	bal.	0.85	0.25	0.028	0.036	0.027	77.41
Extracted Si	0.25	0.027	tr	0.048	0.001	0.004	bal.
Purified Si	0.21	0.008	tr	0.028	0.001	0.003	bal.

Table 3. Percentage of the crude silicon added to the molten aluminium.

Sp. No.	1	2	3	4	5	6
Si% added	30	40	50	60	70	80

Photo. 1 shows the micro-structure of the specimen No. 2 containing 40 per cent of silicon. Here, the primary silicon crystals are grown into large plates, the interspaces being chiefly filled up by eutectic of aluminium and silicon.



(×100)

Photo. 1. Structure of Al-Si alloy containing 40% Si (Sp. No. 2) unetched.

The forms of iron and other impurities enumerated in (1) could not be ascertained, owing to the extremely small contents. Table 2 shows the analyzed composition of these alloys. It is shown that carbon is partially eliminated by alloying.

(ii) Dissolving out aluminium

For the purpose of dissolving out aluminium from these specimens, HCl, HNO_3, H_2SO_4 and NaOH were chosen as solvents, and for expediting the reaction, electrolysis was resorted to by direct current between the specimen as anode and lead plate as cathode.

Figs. 5(A)~(D) show the relations of voltage versus current density in the test with specimen No. 2 as anode and with various concentrations of the above acid solutions. The values of the voltage are those measured after holding the current density at the indicated values for 1 minute. By comparing these curves with one another, it will be seen that when H_2SO_4 or NaOH is used, a point of

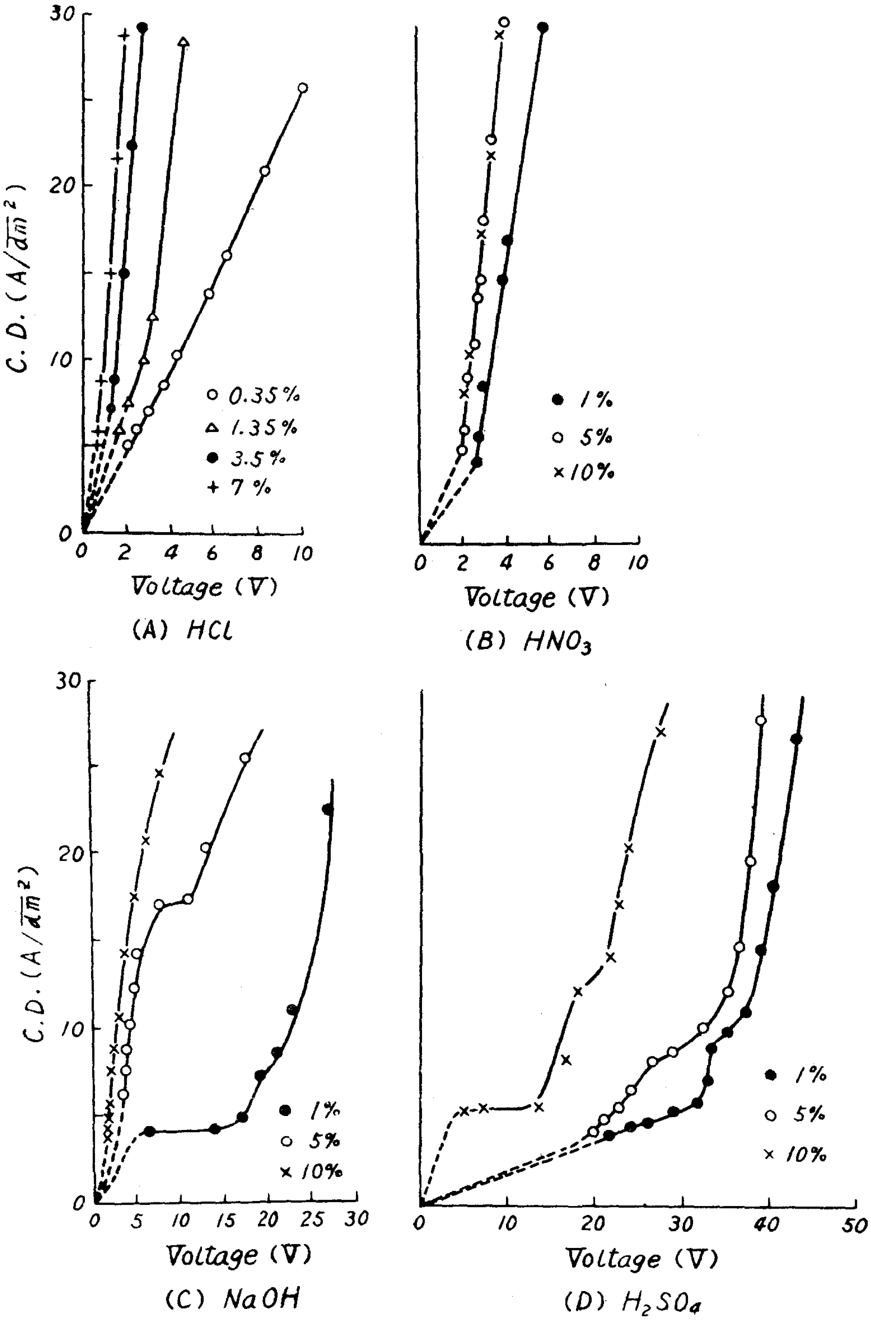


Fig. 5. Current density-voltage curves obtained during the electrolysis of Sp. No. 2 (D. C.)

inflection appears in the curve, indicating the adhesion of oxides or hydroxides on the anode, thereby impeding the flow-out of aluminium. The electrolyte showing a high current density at the minimum voltage was HCl, as shown in Fig. 5(A).

Therefore, HCl was adopted for dissolving aluminium, its concentration being fixed at 3.5 per cent for convenience of operation. Fig. 6 shows the relation of voltage versus current density, when specimen No. 2 was used as anode in the electrolysis under alternating current in 3.5 per cent HCl solution. Here, the current density increases also linearly with the increase in voltage, showing that for dissolving out aluminium alternating current may be used as well.

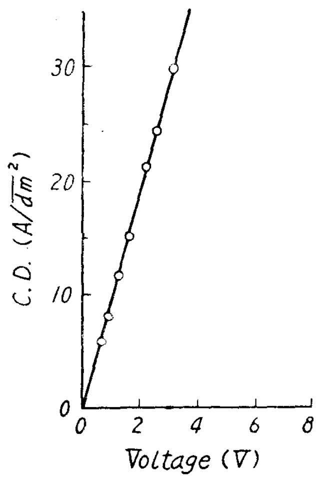


Fig. 6. Current density-voltage curve obtained during the electrolysis of the Sp. No. 2 (A.C.)

Fig. 7 shows the relation of direct current voltage versus current density obtained by varying the composition of Al-Si alloy used as anode. It shows that the curve is little affected by the composition of the anode.

For instance, the conditions adopted in the electrolysis with specimen No. 1 as anode in 3.5 per cent HCl were such as shown in Table 4. By such an electrolysis, silicon was obtained as anode slime.

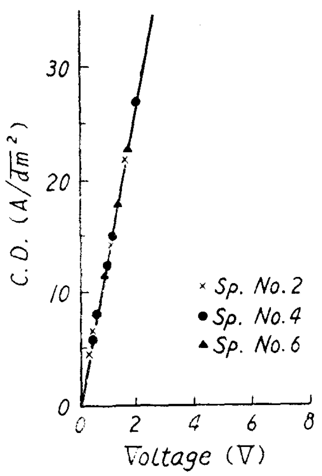


Fig. 7. Curvent density-voltage curve obtained during the electrolysis of Sp. No. 2, No. 4 and No. 6 (D.C.)

Table 4. Example of the electrolysis of Al-Si alloy. (Sp. No. 1)

Anode	
Composition of	Al-30% Si
Initial weight of (A)	170 g
Dissolved weight of	120 g
Electrolyte	3.5% HCl
Conditions of ele:trolysis	
Voltage	4~10 V
Current density	~8.4A/$\overline{dm}^2$
Duration of time of electrolysis	47 hr
Temperature of electrolyte	~90°
Weight of silicon extracts as anode slime	17 g
Weight of silicon after treated with acids (B)	15 g
Yield : $\frac{B}{\text{Wt. of Si in (A)}} \times 100$	30%

(iii) Composition and treatment of slime

The anode slime obtained by the electrolysis under the conditions shown in Table 4 was collected, duly washed and dried, and sifted with a sieve of 20 mesh. The result of analysis of particles thus collected is shown in Table 5, and Photo. 2 shows their actual appearance. From the table it will be seen that the amount of impurities in the larger particles of the anode slime are extremely reduced. The iron content in the crude silicon should remain in the slime in the form of Al-Fe-Si ternary compounds, but owing to the fineness of the crystal size, they probably fail to remain on the sieve.

Table 5. Content of Fe and Al in the silicon obtained as anode slime.

Sp. No.	Fe %	Al %
1	0.02	0.28
2	0.02	0.27
3	0.027	0.25
4	0.023	0.36
5	0.020	0.14
6	0.020	0.10
7	0.021	0.10
8	0.02	0.11
9	0.03	0.49
10	0.033	0.48

Table 6. Content of Fe and Al in the silicon after treated with HF and aqua regia.

Sp. No.	Fe %	Al
1	0.025	0.22
2	0.040	0.29
3	0.016	0.19
4	0.019	0.15
5	0.020	0.16
6	0.017	0.14
7	0.007	0.074
8	0.003	0.18
9	0.016	0.11

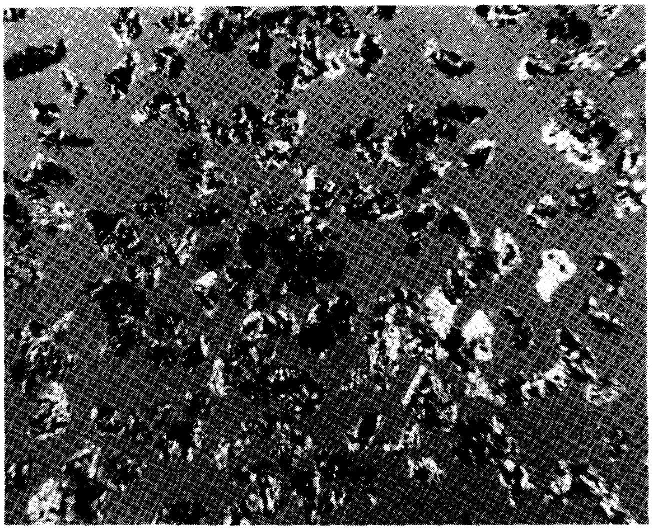

(×10)

Photo. 2. Crystals of silicon extracted as anode slime by electrolysis.

Table 6 shows the changes in the contents of the impurities, iron and aluminium, after treating the anode slime with aqua regia and 10 per cent HF. It is seen that silicon of considerably high purity is produced by this treatment. The result of complete chemical analysis of such a processed sample is shown in Table 2.

(iv) Behaviour of Al-Fe-Si ternary compounds against acid

Specimens of Al-4 per cent Fe-6 per cent Si alloy prepared by melting and slowly cooling from 850 to 500°C in 17 hours were used as anodes in the electrolysis in 3.5 per cent HCl and the slime was collected, from which the Al-Fe-Si ternary compounds were hand-picked. The result of analysis and the actual appearance of these compounds are shown in Table 7 and Photo. 3, respectively.

Table 7. Content of Fe and Si in the ternary compound Al_4FeSi.

No. of Exp.	1	2	3
Fe %	23.90	25.70	25.20
Si %	15.77	17.40	16.70

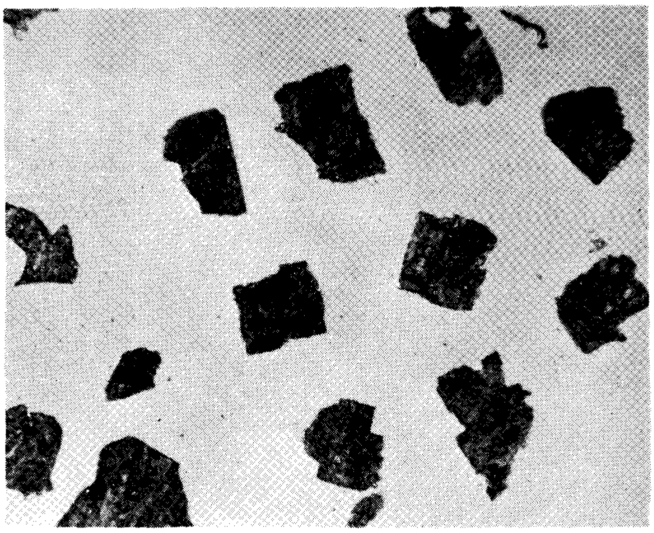

(×16)

Photo. 3. Crystals of Al-Fe-Si ternary intermetallic compound extracted from Al-Fe-Si alloy by electrolysis.

These crystals were placed in hydrochloric acid solutions of various concentrations, and their behavior was observed as follows: They produced bubbles and dissolved in hydrochloric acid of concentration above 7 per cent and in aqua regia and hydrofluoric acid, the bubbling being much stronger.

Thus, it is assured that even if such compounds remain mixed in the anode slime produced in the described process of purifying silicon, a subsequent treatment with acids will effect the removal of such iron-bearing compounds.

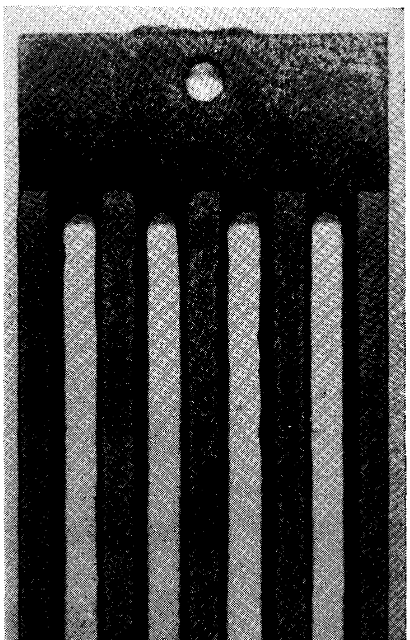


Photo. 4. Electrode used for electrolysis.

3. The process of purification

The above results leads to the adoption of the series of process shown in Fig. 8 in practical application of the new silicon purifying method proposed by the present authors. The total content of impurities except aluminium in the purified silicon can be reduced to less than 0.04 per cent by going through these processes.

II. Semi-industrial test

1. Method

(i) Specimens

The specimens were made of the same crude silicon used in the fundamental researches mentioned above, the chemical composition being shown in Table 8. Commercial purity aluminium was used as the solvent.

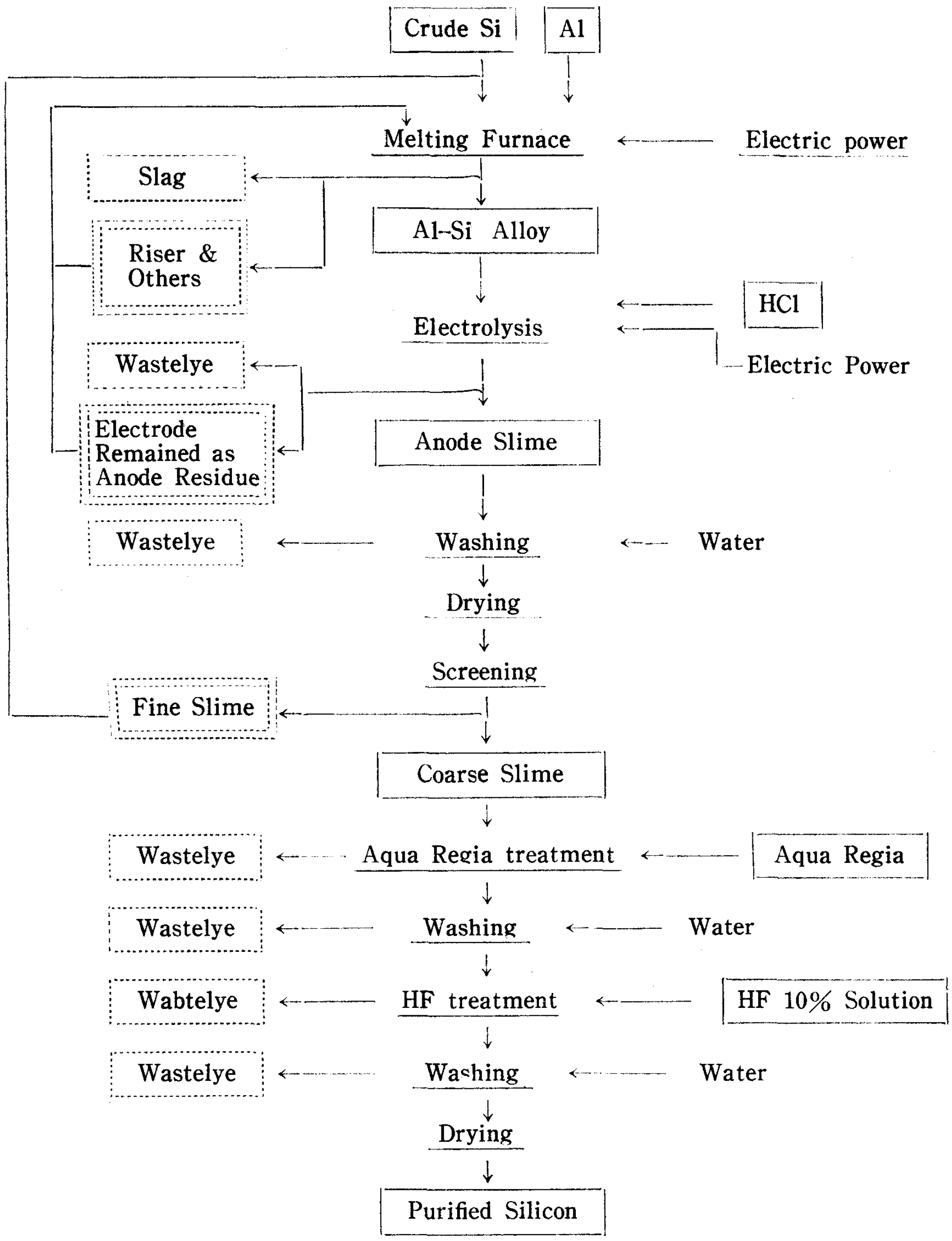


Fig. 8. Flow sheet of the present refining mothod.

Table 8. Composition of crude silicon, extracted and purified silicon.

Materials	Chemical Composition (wt.%)					
	Al	Fe	Ca	C	Ti	P
Crude Si	0.29	0.31	0.29	0.093	0.026	0.012
Si obtained as anode slime	0.93	0.012	tr	0.028	0.001	0.004
Purified Si treated with acid 1	0.18	0.003	tr	0.022	0.001	0.003
Purified Si treated with acid 2	0.22	0.008	tr	0.021	non	0.004

(ii) Method of alloying and preparation of anodes

About 390 g of aluminium was first melted in a graphite crucible No. 5, and when the temperature of the melt rose to 800°, about 290 g in total of silicon was added to it piecemeal. After superheating at 1,000°C, the melt was cast in a dry sand mold preheated at about 200°C, to prepare the anodes. The anodes were, as shown in Photo. 4, of comb-shaped pieces each with 5 teeth of 14 cm in length and of trapezoidal cross-section, 8 mm at the top side, 11 mm at the bottom side and 20 mm in height. 12 such anodes containing 40 per cent of silicon, about 400 g each in weight excluding the residual melt, riser and other unusable odds, were prepared.

Table 9. Electrodes obtained by alloying crude silicon in aluminium. Weight of each change consists 390 g Al and 260 g Si.

No. of exp.	Alloys obtained wt (g)	Alloys obtained %	Electrode obtained wt (g)	Electrode obtained %	Risers and others wt (g)	Risers and others %
1	620	95.4	400	61.5	220	33.7
2	620	95.4	400	61.5	220	33.7
3	620	95.4	400	61.5	220	33.7
4	620	95.4	400	61.5	220	33.7
5	590	90.8	390	60.0	200	33.8
6	590	90.8	390	60.0	200	30.8
7	600	92.3	400	61.5	200	30.8
8	600	92.3	380	58.5	220	30.7
9	580	89.3	380	58.5	200	33.8
10	610	94.9	400	61.5	210	30.6
11	590	90.8	390	60.0	200	32.8
12	620	95.4	400	61.5	220	30.7

(iii) Electrolysis

Glass vats of $11 \times 12 \times 18\ cm^3$ in dimension containing about 1,500 cc of 3.5 per cent HCl were used as electrolyzer. At the centre of the vat was stood the above-mentioned anode of Al-Si alloy and lead plates each of 0.5 mm in thickness were placed on both sides of it as cathodes. No measure was taken for circulating the solution but the method of replenishing the vats with the decrement of the 3.5 per cent HCl solution was adopted throughout the process. The voltage was kept at ca. 2.5 volt per vat and the current at 15~20 A, so that the current density amounted to ca. 4.5 $A/\overline{dm}^2$. The electrolysis was continued for about 17.5 hours, after which the anode slime was collected, washed with running water and dried.

(iv) Treatment of the slime

The dried slime was sieved and larger particles were treated with aqua regia and 10 per cent hydrofluoric acid solution for 24 hours, washed and dried.

2. Results of the test

(i) Loss in melting

The melting loss sustained upon melting crude silicon in molten aluminium amounted only to 5~10 per cent as shown in Table 2, but the rate of recovery of the material as the anode plates was about 60 per cent.

(ii) Electrolysis

Fig. 9 shows the change in voltage and the current density during the electrolysis with 6 unit vats arranged in series. The change in the temperature of the solution is also indicated. According to calculations based on the figure, the total direct consumption of the electric power for the electrolysis in a series of 6 vats amounted to ca. 5.98 KWH.

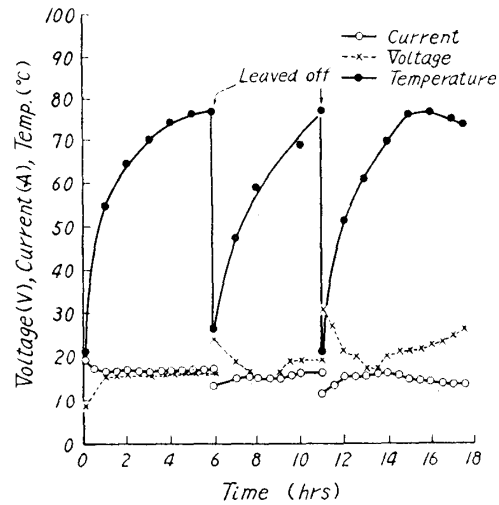


Fig. 9. Change of voltage, current density and temperature of electrolyte during electrolysis.

(iii) Purity of the produced silicon

In Table 8 is shown the composition of the anode slime and the purity of the silicon samples subjected to the treatment with aqua regia and 10 per cent hydrofluoric acid solution. It will be seen that the contents of impurities in the purified silicon are all extremely low, except that of aluminium.

(iv) Recovery of silicon

Table 10 shows the total weight and the recovery rate of anode slime and purified silicon. The final yield of purified silicon amounted to around 30 per cent.

Table 10. Balance sheet obtained by this experiment showing the yield of purified silicon.

Products	Weight (g)	Yield (%)
Total weight of crude silicon used for purification	3,120	—
Total weight of Al used as solvent	4,680	—
Al–40% Si obtained	7,260	93.1
Electrode obtained	4,730	60.6
Risers and others	2,530	32.2
Electrodes dissolved by electrolysis	3,770	—
Electrodes remained as residue	960	12.3
Anode slime obtained	1,670	53.6
above 60 mesh	1,025	32.9
Under 60 mesh	635	20.7
Purified silicon obtained	910	29.2

(v) Cost of purification

Based on the above results of test, the calculated quantity and price of the materials required for manufacturing 1 kg of purified silicon would be as shown in Table 11. Thus, the materials would cost 4,507 yen per kg of purified silicon, but when the undissolved anodes and the remaining chemicals are taken into account, this cost would be further reduced.

Table 11. Quantities and costs of materials required in order to produce 1 kg refined silicon.

Materials	Quantity	Cost	
		Unit price	Total
Crude silicon	3,470 g	240 Yen/kg	833
Al	5,200 g	230 Yen/kg	1,196
35% HCl	4,000 cc	100 Yen/l	400
Aqua Regia	5,000 cc	100 Yen/l	500
HF	500 cc	2,400 Yen/l	1,200
Electric power			
for melting	120 KWH	1.5 Yen/KWH	360
for electrolysis	12 KWH	1.5 Yen/KWH	18
Total amount of cost	—		4,507

Summary

The principle and the method were stated for producing purified silicon as anode slime by melting crude silicon in aluminium as solvent and electrolysing in hydrochloric acid solution with the resultant alloy specimens as anodes for removal of impurities. Then, the behaviors of the individual impurities were subjected to experimental observation, and a new method for purifying silicon was proposed. As the flow-sheet for applying this method to practice, the recommendability of the processes shown in Fig. 8 was experimentally verified.

With the aim of estimating the quantity and the cost of the materials required in practical application of this purifying method, we made a semi-industrial test processing about 3 kg of crude silicon. The chemical composition of the obtained purified silicon was as listed below, the contents of the impurities except aluminium being extremely low.

Al: 0.18 %, Fe: 0.003 %, Ca: Trace, C: 0.022 %,
Ti: 0.001 %, P: 0.003 %

Acknowledgments

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